Controlled Alloy Corrosion: A Method for Creating Self-Defusing Ordnance

Sean G. Corcoran
Department of Materials Science and Engineering
Virginia Polytechnic Institute and State University
213 Holden Hall
Blacksburg, VA 24061-0237

Phone: (540) 231-1898 Fax: (540) 231-8919 E-mail: sgc@vt.edu

Keith Plumadore
Research and Development Department
Naval EOD Technology Division
Indian Head, MD 20640
Phone:(301) 743-6850, Ext.226 Fax:(301) 744-6947

E-mail: plumadore@eodpoe2.navsea.navy.mil

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LONG-TERM GOALS

Explosive ordnance that has been deployed but fails to detonate poses a great concern for engineers charged with the mission of disposal. The long-term goal of this research is to develop timed corrosion mechanisms that can be incorporated into the design of current explosive ordnance as a means of self-defusing dud ordnance.

OBJECTIVES

This proposal is focused on the encapsulation of a liquid environment directly around a key component of the explosive ordnance. Our first phase of this work will look at the encapsulation of a corrosive environment around an electronic wire in fusing circuitry. By controlling the chemistry of the encapsulated environment, we will investigate the feasibility of failing an electronic circuit over long time frames. Our specific objective is to develop feasible environment systems for the controlled failure of encapsulated copper electronic wire at time frames of three months, six months, and one year.

APPROACH

There are basically two main directions in which "timed" defusing of explosive ordnance can be addressed from a corrosion approach. The first is the continual exposure of the metallic part to the environment from the date of manufacture and the second is to expose the part to the environment at some later predetermined time. The first method requires the design of the component to undergo a slow corrosion process that requires anywhere from six months to two years to cause failure depending on the ordnance. The second method would be a very rapid corrosion process resulting in failure within days or weeks after delayed exposure to the corrosive environment. For example, the corrosive environment could be "released" upon deployment of the device. This phase of the project is focused on the first approach (slow continual corrosion process).

Depending upon the specifics of the explosive ordnance, a variety of critical components of a fusing mechanism could be identified as candidates for encapsulation within a corrosive environment. We have chosen to focus on the timed failure of copper electronic wire as shown schematically in Figure 1. Through the choice of the environment chemistry, we can control the rate of copper corrosion. However, since we are dealing with a self-contained environment, the corrosion process itself will result in a continual change in the environment chemistry. These changes will result in a continual change in the corrosion rate of the copper over the duration of the exposure. However, these changes should be quantifiable and predictable. As discussed further below in the RESULTS section, we are also looking at maintaining a constant corrosion rate by taking advantage of passivation reactions for copper corrosion. Graduate student, Dylan Pugh, and the Principal Investigator are conducting this research

Encapsulated environment Cu²⁺ 2Rⁿ⁺ 2R⁽ⁿ⁻¹⁾⁺ Cu wire Corrosive Failure of the wire

Figure 1. Encapsulation of a corrosive environment around copper electronic wire will allow us to time open-circuit failure. The corrosion of the copper will be controlled by the chemistry of the environment, the presence of redox species, R^{n+} , and the length of the exposed copper.

WORK COMPLETED

- The corrosion rate of copper has been measured in a variety of corrosive environments.
- Computer code was developed to predict the change in corrosion rate during the long-term corrosion of copper in confined cells.
- An encapsulation procedure has been developed for the long-term evaluation of copper corrosion in a geometry consistent with that in Figure 1.
- Short-term encapsulated systems were tested as proof of concept.

Details of the above are explained in the next section.

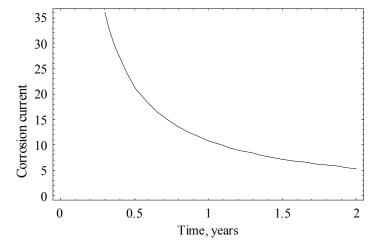
RESULTS

Our first series of measurements were conducted on copper alloys rather than pure copper. The corrosion of Cu-30at% Zn undergoes selective dissolution of Zn in ammonia containing electrolytes. This de-alloying process leaves behind a porous, brittle film of copper that results in massive cracking

of the alloy. Although this system provides for catastrophic failure of the device, it was not pursued any further because the failure times were too short (days to weeks) and the system generated H₂ gas. Gas generation leads to pressure changes in our encapsulated cell and will be a problem for a long-term corrosion approach. However, this system does have great promise if we delay the introduction of the corrosive environment into the cell and then require rapid failure of the device. Although not part of this phase of the project, we may pursue this system in the future especially as pertaining to other copper alloy components in explosive ordnance.

At this stage, we decided to focus on the corrosion of pure copper where the generation of H_2 gas is not thermodynamically favorable, i.e., the copper oxidation potential is positive of the hydrogen reduction reaction. Short-term failure tests were performed in sulfuric acid as proof of concept. In a 0.2 ml encapsulated electrolyte of 1 M $H_2SO_4 + 0.169$ M Fe^{3+} , we achieved complete failure of a 0.25 mm Cu wire in 24.5 hours. This data was also used as input into a Mathematica model to predict the feasibility of using activated copper corrosion for long-term failure. As the corrosion process continues in a confined cell, the concentration of Cu^{2+} and Fe^{2+} increases and the concentration of Fe^{3+} decreases. This results in the continual shifting of the corrosion rate. The model calculates changes in anodic and cathodic reactions and assumes Tafel behavior. However, we require input for the change in exchange current densities with concentration. Using the short-term tests as input to our model for the exchange currents, we find that this approach is best for failure times on the order of days to weeks.

Another approach to the corrosion of copper that should allow us to maintain a steady state corrosion rate is to drive the copper corrosion in the passive region in mildly alkaline electrolytes. Assuming a constant corrosion current density and a decreasing exposed surface area (resulting from the thinning of the wire), we find that the predicted time of failure decreases as the inverse of the corrosion rate as shown in Figure 2.



Failure	Corrosion
Time	Rate
(months)	$(\mu A/cm^2)$
3	43
6	22
12	11

Figure 2. Calculation of the Steady State Corrosion Current Needed for the Indicated Failure Times. The Calculation was made for a 0.25 mm Diameter Copper Wire.

From this calculation, we find that we need a steady-state corrosion rate of approximately 40, 20, and $10 \,\mu\text{A/cm}^2$ for three, six, and 12 month failure times. One electrolytic environment that looks promising for such low corrosion rates is the system $0.082M \, \text{Na}_2\text{CO}_3 + 0.018M \, \text{Na}_3\text{HCO}_3$. The Polarization behavior for Cu in this system is shown in Figure 3. As shown, the passivation current in

this system is less than $10 \,\mu\text{A/cm}^2$. By altering the composition of this electrolyte, we hope to tailor the long-term corrosion rate within the appropriate range. Other weakly alkaline electrolytes are also being explored. Once the proper corrosion rates have been achieved, long-term encapsulated cells will be tested for reproducibility.

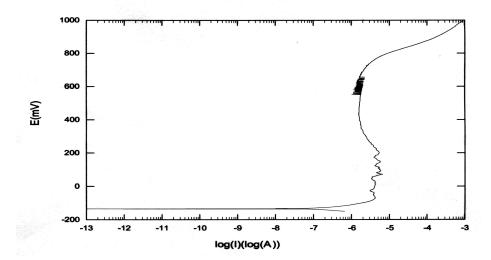


Figure 3. Polarization Behavior of Cu in 0.082M Na₂CO₃ + 0.018M NaHCO₃ Displaying a Passivation Current of Less Than $10 \mu A/cm^2$.

IMPACT/APPLICATIONS

If successful, this project will provide weapons designers with a means of incorporating passive (i.e., no demands for electrical power) defusing systems to minimize the threat posed by "dud" ordnance after hostilities cease. This has potential application for both EOD personnel conducting UXO operations and indigenous populations (humanitarian demining).

In addition this project has impact in the advancement of our understanding in the area of long-term corrosion. Knowledge gained, as a result of this effort, might also be applicable to those areas of interest involving passively controlled mechanical timing and/or movement.

TRANSITIONS

All results obtained from this project are being directly transferred to the Naval Explosive Ordnance Technology Division in Indian Head, MD through personal meetings every two months and through a written monthly reporting process. If successful, it is anticipated that the knowledge gained and the systems developed in this research will be transitioned to the weapons development community.

RELATED PROJECTS

There is one project closely related to this effort. This project is also an ONR grant to Virginia Polytechnic Institute and State University and is entitled "Mine Deactivation Through a Binding Interlayer". This project's Principal Investigator is Dr. Brian Love who is striving to achieve the same objective as this one, but by means of long-curing adhesives rather than corrosives.